Pressure-Induced Metal-to-Ligand Electron Transfer and the Electrical Conductivity of Some Pt(II)-Glyoximes[†]

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Mid-infrared (900—1600 cm^{-1}), visible absorption spectra and electrical resistance of bis(benzil dioximato)-platinum(II) [abbreviated as Pt(bz)$_2$], bis(dimethylglyoximato)platinum(II) [Pt(dmg)$_2$], bis(1,2-cyclohexanedione dioximato)platinum(II) [Pt(cd)$_2$], and bis(pyruvaldehyde dioximato)platinum(II) [Pt(pa)$_2$] have been measured at high pressures. A decrease of the C=N frequency by -40.0 cm^{-1}, with reduction of the $d\pi \to \pi^*$ optical transition intensity by $\simeq 14\%$, show that [Pt(bz)$_2$] enhances thermally its $d\pi \to \pi^*$ electron transfer at high pressures up to 35 kbar. No such changes are observed for [Pt(dmg)$_2$], [Pt(cd)$_2$], and [Pt(pa)$_2$]. This backbonding causes [Pt(bz)$_2$] to release the instability, due to increasing overlapping of the electron clouds around Pt(II) at high pressures, that is the cause of the resistance minimum.

Many one-dimensional Pt(II) complexes exhibit minima of electrical resistance at high pressures.[1–4)] These minima can be explained by calculations that identify two opposing effects on the $5d_{z^2}$—$6p_z$ energy gap. Compression of Pt–Pt separations to as little as 2.80 Å increases the $5d_{z^2}$—$6p_z$ overlap, decreasing the band gap,[5,6)] while compression of the Pt-ligand separation usually increases the band gap as a result of ligand π-Pt p_z and ligand σ-Pt $\sigma(d_{x^2-y^2})$ interactions.[6)] Exceptions to these generalizations are known. MgPt(CN)$_4$·7H$_2$O has no detectable resistance minimum.[1)] The behavior of MgPt(CN)$_4$·7H$_2$O has been interpreted as the result of an additional electronic effect, strong enhancement of Pt $d\pi$-ligand π^* backbonding with compression, which reduces Coulombic repulsions between electrons in Pt orbitals, including orbitals on adjacent Pt atoms.

In a previous paper, Hara et al reported the electrical behavior under high pressure of several Pt(II) one-dimensional solids, including bis(benzil dioximato)platinum(II) [as Pt(bz)$_2$], bis(dimethylglyoximato)platinum(II) [as Pt(dmg)$_2$], bis(1,2-cyclohexanedione dioxomato)platinum(II) [as Pt(cd)$_2$], and bis(pyruvaldehyde dioximato)platinum(II) [as Pt(pa)$_2$].[2)] When polycrystalline [Pt(dmg)$_2$] is compressed, its resistance decreases continuously, by as much as 16 orders of magnitude, to 40 kbar; further compression causes the resistance to increase. [Pt(bz)$_2$], however, has no resistance minimum; compression to 150 kbar continuously decreases its resistance, by as much as 13 orders of magnitude. In this respect, the high pressure electrical characteristics of [Pt(bz)$_2$] resemble those of MgPt(CN)$_4$·7H$_2$O.

Since the pressure dependence of the C=N stretching vibration and $d\pi \to \pi^*$ optical transition of [Pt(bz)$_2$] could be measured with our optical apparatus, we sought to establish whether the pressure dependence of the relevant spectra provided direct evidence that enhancement of the $d\pi \to \pi^*$ thermal electron transfer was responsible for the atypical resistance characteristics of [Pt(bz)$_2$]. For comparative purposes, infrared and visible absorption spectra of [Pt(dmg)$_2$], [Pt(cd)$_2$], and [Pt(pa)$_2$], which have distinct resistance minima, also were studied. Compression of [Pt(bz)$_2$] to 35 kbar had two effects on its spectra, the wavenumber of one C=N stretching band of the infrared spectrum decreased by an unusually large amount, and the intensity of the visible $d\pi \to \pi^*$ absorption band diminished. No such changes were observed for [Pt(dmg)$_2$] or the other comparison compounds. The former effect indicates that metal-to-ligand $d\pi \to \pi^*$ thermal electron transfer in the ground state, which reduces the $d\pi \to \pi^*$ optical transition intensity, is greatly enhanced by compression of [Pt(bz)$_2$], and demonstrate that enhancement of $d\pi \to \pi^*$ backbonding by electron acceptors such as the four phenyl groups of [Pt(bz)$_2$] can be an important factor for reducing the electron repulsion terms on the Pt chain and increasing the conductivity of one-dimensional Pt complexes.

Experimental

For the infrared and visible spectral measurements, pressures to 35 kbar were generated by means of a high presuure optical bomb using a NaCl pressure medium.[7)] The infrared technique has been described elsewhere,[8)] except that these measurements were performed with a Perkin-Elmer 421 infrared double-beam spectrometer and were carried out in the range 900—1600 cm^{-1}. The visible spectral measurement was performed with a Bausch-Lomb grating spectrometer. The polycrystalline materials studied were prepared by the method used in the previous work.[2)] The molecular structures of these samples are illustrated in Fig. 1.

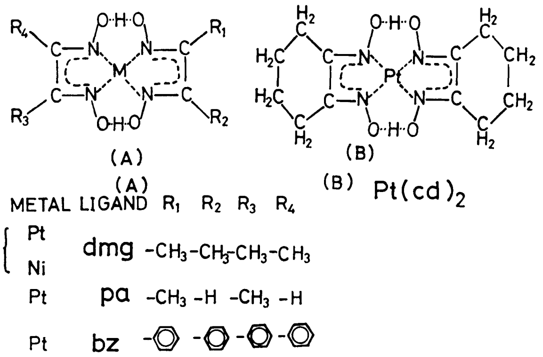

Fig. 1. Molecular structure of the samples.
(A) Bis(dimethylglyoximato)platinum(II) and nickel-(II); bis(pyruvaldehyde dioximato)platinum(II); bis(benzil dioximato)platinum(II).
(B) Bis(1,2-cyclohexanedione dioximato)platinum(II).

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Results and Discussion

Figure 2 shows the effect of pressure on the electrical resistance of [Pt(bz)$_2$], [Pt(pa)$_2$], [Pt(cd)$_2$], and [Pt-(dmg)$_2$]. These effects are reversible and reproducible. The electrical resistance of [Pt(dmg)$_2$], [Pt(cd)$_2$] and [Pt(pa)$_2$] show sharp resistance minima at 40, 90, and 120 kbar, respectively.

Infrared spectra of [Pt(dmg)$_2$] at 0, 17, and 35 kbar are shown in Fig. 3. The C=N stretching modes are located at 1534 and 1482 cm^{-1}, and the N–O stretches at 1249 and 1078 cm^{-1}. The splitting of the C=N modes in [Pt(dmg)$_2$] derives from the unequal C=N distance, 1.27 and 1.38 Å, respectively.[9] By way of comparison, [Ni(dmg)$_2$] has single C=N stretching mode (1562 cm^{-1}) since its two distances are essentially identical, 1.30 and 1.29 Å.[10] Although the pressure effects are small, two are noteworthy. The C=N mode at 1482 cm^{-1}, corresponding to the 1.38 Å bond, disappears over 17 kbar, leaving single mode at 1533 cm^{-1}; this trend also is observed for [Pt(cd)$_2$] and [Pt(pa)$_2$]. Also the degenerate and symmetric deformation modes of C–CH$_3$ between 1447—1330 cm^{-1} do not change much; thus, hyperconjugation must be less important than has been suggested.[2]

Comparable parts of the infrared spectra of [Pt(bz)$_2$] at several pressures are reproduced in Fig. 4. Since two stretching bands are observed (at 1382 and 1430 cm^{-1}), the two C=N distances must be different. That these

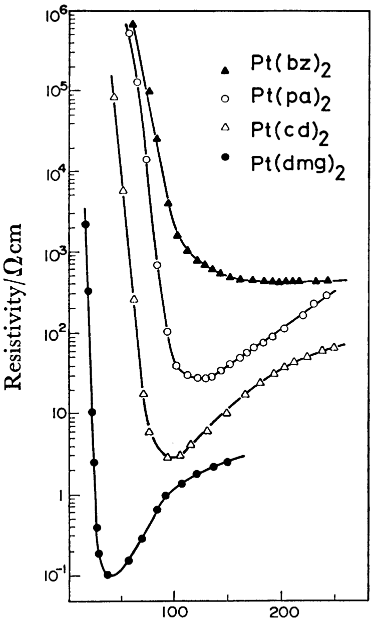

Fig. 2. Pressure effect on the electrical resistance of [Pt(bz)$_2$], [Pt(pa)$_2$], [Pt(cd)$_2$], and [Pt(dmg)$_2$].

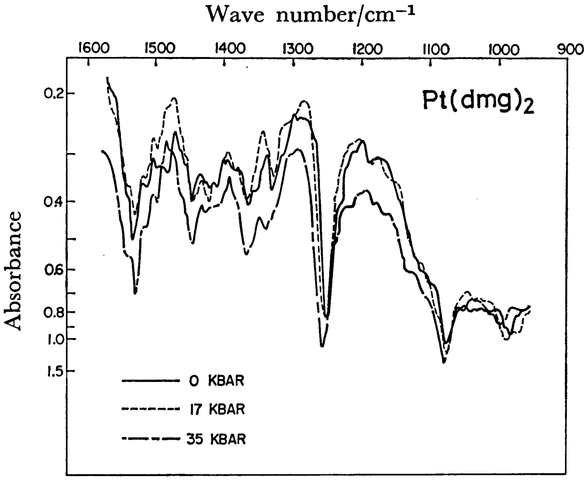

Fig. 3. Infrared spectra of [Pt(dmg)$_2$] at 0, 17, and 35 kbar.

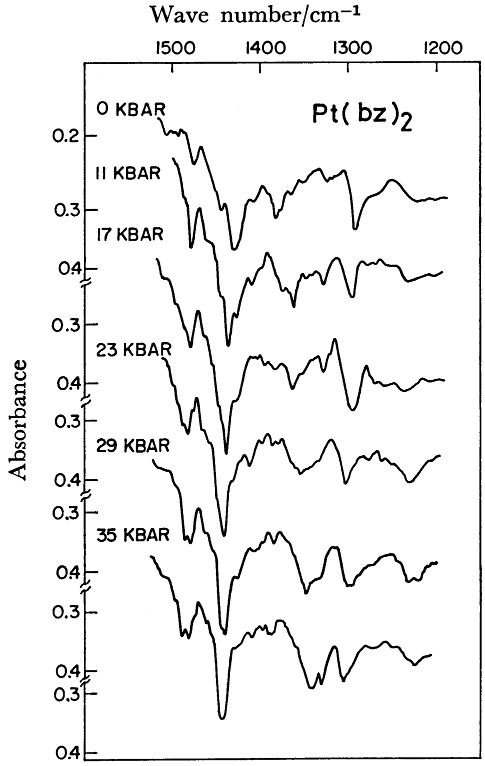

Fig. 4. Parts of the infrared spectra of [Pt(bz)$_2$] at several pressures.

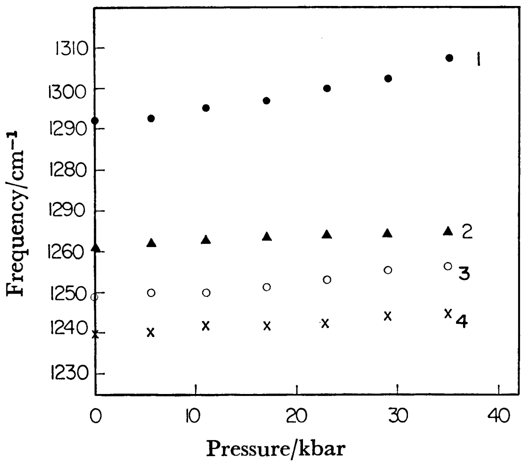

Fig. 5. Pressure-induced shifts of the N-O stretching bands of 1: [Pt(bz)$_2$], 2: [Pt(pa)$_2$], 3: [Pt(dmg)$_2$], and 4: [Pt(cd)$_2$].

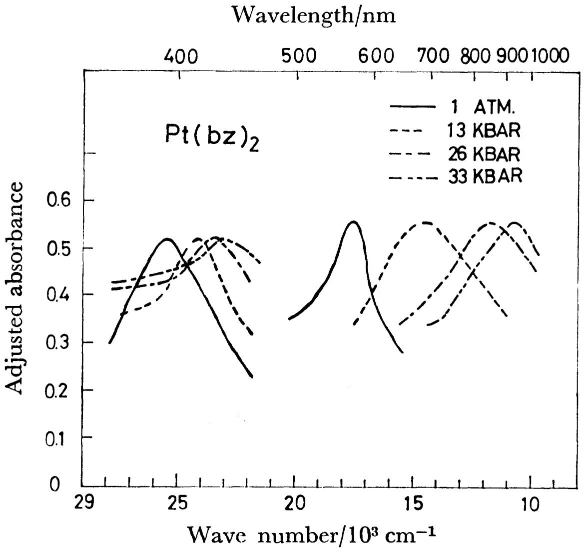

Fig. 6. Pressure dependence of the visible absorption spectra of [Pt(bz)$_2$].
----: The peak intensities at higher pressures are normalized to the corresponding ones at 1 atm.

bands, and similar bands of [Pt(dmg)$_2$], [Pt(cd)$_2$], and [Pt(pa)$_2$], have different pressure dependence is easily understood if one considers that the lower frequency band corresponds to the longer, more compressible C=N bond. However, this interpretation does not explain the anomalous shift of the 1382 cm^{-1} band to lower wavenumbers, by -40 cm^{-1} in 35 kbar. It is known that the frequencies of C=N stretching modes of metal-glyoximes decrease with increasing metal-to-ligand ($d\pi \rightarrow \pi^*$) backbonding.[11] The large frequency reduction of the C=N modes of [Pt(bz)$_2$] suggests that $d\pi \rightarrow \pi^*$ backbonding is greatly enhanced at high pressures. As can be seen in Fig. 5, only small pressure-induced shifts of the N–O stretching bands (as well as C=N bands) are observed for [Pt(dmg)$_2$], [Pt(cd)$_2$], and [Pt(pa)$_2$], indicating that backbonding is very minor in these complexes.

The pressure dependence of the visible absorption spectra of [Pt(bz)$_2$], shown in Fig. 6, also indicates the importance of $d\pi \rightarrow \pi^*$ backbonding in this compound. Both the 25.4 kK band ($d\pi \rightarrow \pi^*$ charge transfer[12]) and the 18.0 kK band ($5d_{z^2} \rightarrow 6p_z$) shift to lower wavenumbers with compression, by -67 and -208 cm$^{-1}\cdot$kbar^{-1} respectively. However, the $\simeq 14\%$ decrease of the intensity of the 25.4 kK band appears more significant; no similar fadeout of the $d\pi \rightarrow \pi^*$ transition is observed for [Ni(dmg)$_2$] or [Pt(dmg)$_2$].[13,14] This diminishing intensity is caused, in the ground state at high pressures, by occupation of ligand π^* orbitals by $d\pi$ electrons from the Pt atom. Thus, the four phenyl groups in [Pt(bz)$_2$], which withdraw π-electrons from the C=N bonds, also induce significant electron transfer from the Pt $d\pi$ orbital to the ligand π system. In [Pt(bz)$_2$], the central Pt(II) can compensate for the increasing overlap of the electron clouds at high pressures; which is the cause of the resistance minimum, by removing electrons outwards to the edge of the plane of the complex. These observations suggest that, by selecting even better electron acceptors than phenyl, one could make Pt-complexes that are significantly more conductive than [Pt(bz)$_2$].

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